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# UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No.: Mo-5451/LeA 33,624

First Inventor or Application Identifier: Christoph Gürler

Title: METATHESIS IN THE PRESENCE OF IONIC

Express Mail Label No. EK243950065US

## APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

1.  Fee Transmittal Form (e.g., PTO/SB/17)  
(Submit an original and a duplicate for fee processing)

2.  Specification [Total Pages 27]  
(preferred arrangement set forth below)
 

- Descriptive title of the Invention
- Cross References to Related Applications
- Statement Regarding Fed sponsored R & D
- Reference to Microfiche Appendix
- Background of the Invention
- Brief Summary of the Invention
- Brief Description of the Drawings (if filed)
- Detailed Description
- Claim(s)
- Abstract of the Disclosure

3.  Drawing(s) (35 U.S.C. 113) [Total Sheets  ]

4. Oath or Declaration [Total Pages 2]
 

- a.  Newly executed (original or copy)
- b.  Copy from a prior application (37 C.F.R. § 1.63(d))  
(for continuation/divisional with Box 16 completed)
  - i.  DELETION OF INVENTOR(S)  
Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

\*NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATUS IS REQUIRED (37 C.F.R. § 1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).

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Washington, DC 20231

5.  Microfiche Computer Program (Appendix)

6. Nucleotide and/or Amino Acid Sequence Submission  
(if applicable, all necessary)
 

- a.  Computer Readable Copy
- b.  Paper Copy (identical to computer copy)
- c.  Statement verifying identity of above copies

## ACCOMPANYING APPLICATION PARTS

7.  Assignment Papers (cover sheet & document(s))

8.  37 C.F.R. § 3.73(b) Statement  Power of  
(when there is an assignee)  Attorney

9.  English Translation Document (if applicable)

10.  Information Disclosure Statement (IDS)/PTO-1449  Copies of IDS  
Citations

11.  Preliminary Amendment

12.  Return Receipt Postcard (MPEP 503)  
(Should be specifically itemized)
 

- \* Small Entity  Statement filed in prior application.
- 13.  Statement(s)  Status still proper and desired  
(PTO/SB/09-12)
- 14.  Certified Copy of Priority Document(s)  
(if foreign priority is claimed)
- 15.  Other: .....  
.....

16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment

Continuation  Divisional  Continuation-in-part (CIP) of prior application No: \_\_\_\_\_

Prior application information: Examiner \_\_\_\_\_

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

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Mo5451  
LeA 33,624

METATHESIS IN THE PRESENCE OF IONIC LIQUIDS

BACKGROUND OF THE INVENTION

5 The present invention relates to a process for preparing cyclic and/or polymeric compounds by metathesis of starting materials that contain at least two functional groups in the form of substituted or unsubstituted alkene or alkyne units.

For the purposes of the present invention, the term "metathesis" 10 refers to a mutual transalkylidenation of alkenes and alkynes in the presence of catalysts. Reactions of this type are employed in many industrially important processes. A review may be found in: M. Schuster, S. Blechert, Angew. Chem. 1997, 109, 2124 and S. Armstrong, J. Chem. Soc., Perkin Trans. 1, 1998, 371. Metathesis reactions include the 15 oligomerization and polymerization of acyclic dienes (ADMET) and the synthesis of carbocycles and heterocycles having various ring sizes by ring closing metathesis (RCM). Crossed metatheses of different alkenes are also known (Brümmer, O. et al. Chem. Eur. J. 1997, 3, 441).

For the above-mentioned metathesis reactions, it is possible to use 20 the ruthenium-alkylidene compounds described in WO-A-93/20111, the ruthenium-based catalyst systems described by A.W. Stumpf, E. Saive, A. Deomceau and A. F. Noels in J. Chem. Soc., Chem. Commun. 1995, 1127-1128, or the catalyst systems described by P. Schwab, R. H. Grubbs and J. W. Ziller in J. Am. Chem. Soc. 1996, 118, 100 (see also WO 25 96/04289) as catalysts.

The use of nonaqueous ionic liquids for metathesis reactions has 30 recently been described. These ionic liquids are salts or mixtures of salts that are liquid over a wide temperature range. The advantage of ionic liquids is that they are immiscible with aliphatic hydrocarbons. In organic reactions for which the use of a catalyst is necessary, heterogeneous

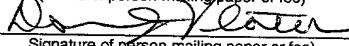
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catalysis can be achieved by addition of ionic liquids and a suitable catalyst that dissolves only or preferentially in the ionic liquid.

U.S. Pat. No. 5,104,840 describes the use of such mixtures as solvents for transition metal complexes, especially nickel complexes that contain no carbon-nickel bonds.

EP-B-448445 describes the use of ionic liquids for the dimerization of unsubstituted monoolefins using nickel chloride. However, a disadvantage here is the use of organoaluminium halide, especially the pyrophoric dichloroethylaluminium, for preparing the ionic liquid.

U.S. Pat. No. 5,525,567 describes the use of ionic liquids for the disproportionation of unsubstituted monoolefins using tungsten catalysts. Here too, it is necessary to use an organoaluminium halide, preferably the pyrophoric dichloroethylaluminium, for preparing the ionic liquid.

EP-A-882691 describes the use of ionic liquids for the dimerization of unsubstituted monoolefins in the presence of nickel chloride. Apart from the pyrophoric dichloroethylaluminium that is used here too, a further disadvantage is that the excess of the Lewis acid aluminium chloride in the ionic liquid results in an acidic reaction mixture.

The above-described metathesis processes are, moreover, suitable only for the reaction of unsubstituted monoolefins, i.e. very simple organic molecules. These processes are not suitable for the reaction of multiply substituted starting materials bearing functional groups, since the catalysts described there cannot be employed or the ionic liquids are unsuitable for other catalysts because of their composition or the fact that the reaction mixture has an acidic character.

It is an object of the present invention to provide a universally usable process for the metathesis of starting materials that contain at least two functional groups in the form of alkene or alkyne units that is carried out using ionic liquids. The process should also be able to be used for substituted alkenes or alkynes.

### SUMMARY OF THE INVENTION

The invention, meeting the above-named object, provides a process that subjects starting materials that contain at least two functional groups in the form of alkene or alkyne units to metathesis. The process is carried out using ionic liquids. Advantageously, the process can be used for substituted alkenes or alkynes. These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description and appended claims.

### DESCRIPTION OF THE INVENTION

10 We have found a process for preparing cyclic and/or polymeric compounds by metathesis of starting materials that contain at least two functional groups in the form of substituted or unsubstituted alkene or alkyne units in the presence of one or more homogeneous or heterogeneous catalysts, wherein the metathesis is carried out in the presence of 15 ionic liquids and the catalysts used are transition metal carbenes or transition metal compounds that form transition metal carbenes under the reaction conditions or transition metal salts in combination with an alkylating agent.

20 It has surprisingly been found that the presence of ionic liquids in the metathesis reaction of starting materials that contain at least two functional groups in the form of substituted or unsubstituted alkene or alkyne units leads to an increase in the operating life of the catalyst since it can be used in the ionic liquid for further metathesis reactions.

25 In a preferred embodiment, the present invention makes it possible to prepare carbocyclic or heterocyclic compounds having ring sizes of  $\geq 5$  ring atoms, including medium-sized rings (from 8 to 11 ring atoms) and large rings ( $\geq 12$  ring atoms) and/or polymeric compounds that can be homopolymers, copolymers or block copolymers.

30 In ring closing metathesis reactions, the ring-closure reaction competes with polymerization. If this reaction is carried out using starting

materials that contain at least two functional groups in the form of alkene or alkyne units, it results in mixtures of cyclic compounds and polymers.

The formation of cyclic compounds is favoured by carrying out the reaction in organic solvents at high dilution or by addition of relatively large volumes of ionic liquids. This applies particularly to the preparation of medium-sized rings (from 8 to 11 ring atoms) and large rings ( $\geq 12$  ring atoms).

The large reaction volumes of organic solvents required to achieve the necessary high dilution limit the maximum space-time yields. Separating off the products after the reaction is complete requires time-consuming separation operations such as chromatography and usually leads to irreversible deactivation of the catalyst used.

The use of relatively large volumes of ionic liquids does, however, allow the desired products to be separated off easily, since they are present in the organic phase that is not miscible with the ionic liquid. If a catalyst that dissolves exclusively or preferentially in the ionic liquid is selected, the deactivation of the catalyst after the work-up can be avoided and the phase comprising the ionic liquid and the catalyst can be used for further metathesis reactions.

In the process of the invention, preference is given to using starting materials that contain, apart from the functional groups participating in the metathesis reaction, at least one further substituent that is inert in the metathesis reaction and/or a heteroatom. These substituents or heteroatoms can be selected independently from among: branched or unbranched alkyl radicals, aromatic or non-aromatic carbocyclic rings, carboxylic acids, esters, ethers, epoxides, silyl ethers, thioethers, thioacetals, anhydrides, imines, silylenol ethers, ammonium salts, amides, nitriles, perfluoroalkyl groups, geminal dialkyl groups, alkynes, alkenes, halogens, alcohols, ketones, aldehydes, carbamates, carbonates, urethanes, sulphonates, sulphones, sulphonamides, nitro groups,

organosilane units, metal centres and oxygen-, nitrogen-, sulphur- and/or phosphorus-containing heterocycles.

The process of the invention is particularly preferably carried out using, as starting materials,  $\alpha,\omega$ -dienes that may contain at least one further substituent that is inert in the metathesis reaction and/or a heteroatom. These substituents or heteroatoms may be selected independently from among branched or unbranched alkyl radicals, aromatic or non-aromatic carbocyclic rings, carboxylic acids, esters, ethers, epoxides, silyl ethers, thioethers, thioacetals, anhydrides, imines, silylenol ethers, ammonium salts, amides, nitriles, perfluoroalkyl groups, geminal dialkyl groups, alkynes, alkenes, halogens, alcohols, ketones, aldehydes, carbamates, carbonates, urethanes, sulphonates, sulphones, sulphonamides, nitro groups, organosilane units, metal centres and oxygen-, nitrogen-, sulphur- and/or phosphorus-containing heterocycles.

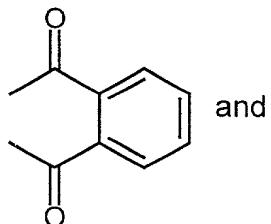
In particular, the process of the invention is carried out using, as starting materials,  $\alpha,\omega$ -dienes that bear a substituent  $NRR^1$  in the  $\alpha$  position to a double bond, wherein

$R$  is an organic substituent, preferably hydrogen, fused or unfused aryl, alkyl,  $CN$ ,  $COOR^2$  or halogen,

$R^1$  is tert-butyl,  $P(R)_2$ ,  $P(R^2)_2$ ,  $COR$ ,  $SO_2PhR$ ,  $COOR$  or  $CONRR^2$ ,

$R^2$  is alkyl or phenyl,

$R$  and  $R^1$  together form

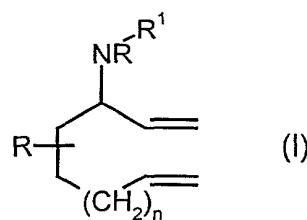


and

said  $\alpha,\omega$ -dienes may also bear at least one further substituent  $R$  in any other position in the molecule with the exception of the  $\alpha$  position.

Use of these dienes as starting materials in the process of the invention makes it possible to obtain cyclic and/or polymeric compounds that bear a substituent  $\text{NRR}^1$ , wherein  $\text{R}$  and  $\text{R}^1$  are as defined above, in the  $\alpha$  position to the double bond.

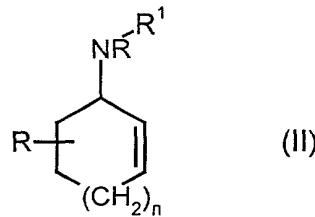
5        In a particularly preferred embodiment, the above-mentioned  $\alpha,\omega$ -dienes are compounds of the formula (I)



wherein  $\text{R}$ ,  $\text{R}^1$  and  $\text{R}^2$  are as defined above and

10      n        is 1, 2, 3 or 4, preferably 1 or 2, particularly preferably 1.

When using compounds of the formula (I), the process of the invention preferably gives cyclic compounds of the formula (II),



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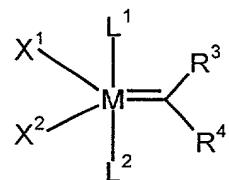
wherein  $\text{R}$ ,  $\text{R}^1$ ,  $\text{R}^2$  and  $n$  are as defined above and the double bond may also be substituted by at least one radical  $\text{R}$ , and/or polymeric products.

Starting materials that are very particularly preferably used in the process of the invention are diallylamine or 3-amino-1,7-octadiene, particularly preferably in their N-carboxymethyl-protected form, or 1,7-octadiene, 10-undecenoyl-allylamine, 1,4-bis-oxypropen-2-yl-but-2-ine or buten-4-yl 10-undecenoate.

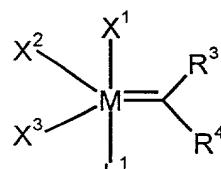
It is also possible to use mixtures of starting materials in the process of the invention. In this case, the starting materials can be added as a mixture to the reaction medium or else can be added sequentially to the reaction medium.

5 In the process of the invention, the catalysts or catalyst precursors used are transition metal carbenes or transition metal compounds that form transition metal carbenes under the reaction conditions or transition metal salts in combination with an alkylating agent. These catalysts can be either ionic or nonionic.

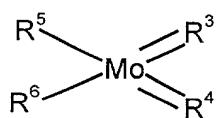
10 The process of the invention is preferably carried out using catalysts of the formulae (III) to (VI), wherein M is ruthenium or osmium, preferably ruthenium.



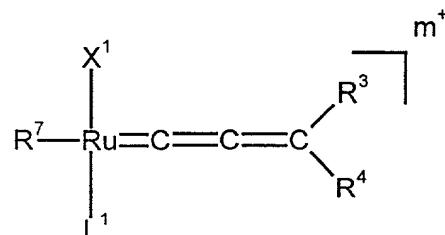
(III)



(IV)



(V)



(VI)

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R<sup>3</sup> to R<sup>7</sup> are radicals that can be selected independently from among hydrogen, C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>3</sub>-C<sub>8</sub>- cycloalkyl, C<sub>2</sub>-C<sub>20</sub>-alkenyl, C<sub>2</sub>-C<sub>20</sub>-alkinyl, C<sub>6</sub>-C<sub>18</sub>-aryl, C<sub>1</sub>-C<sub>20</sub>-carboxylate, C<sub>1</sub>-C<sub>20</sub>-alkoxy, C<sub>2</sub>-C<sub>20</sub>-alkenyloxy, C<sub>2</sub>-C<sub>20</sub>-alkinyloxy, C<sub>6</sub>-C<sub>18</sub>-aryloxy, C<sub>2</sub>-C<sub>20</sub>-alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub>-alkylthio, C<sub>1</sub>-C<sub>20</sub>-alkylsulphonyl or C<sub>1</sub>-C<sub>20</sub>-alkylsulphinyl, N-aryl; in each case unsubstituted or substituted by C<sub>1</sub>-C<sub>12</sub>- alkyl,

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perfluoroalkyl, halogen, C<sub>1</sub>-C<sub>5</sub>-alkoxy or C<sub>6</sub>-C<sub>18</sub>-aryl. The radicals R<sup>3</sup> to R<sup>7</sup> may be linked to one another in cyclic compounds.

X<sup>1</sup> to X<sup>3</sup> are anionic ligands that may be selected independently, in particular F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, CN<sup>-</sup>, SCN<sup>-</sup>, R<sup>3</sup>O<sup>-</sup>, R<sup>3</sup>R<sup>4</sup>N<sup>-</sup>, (R<sup>3</sup>-R<sup>7</sup>)-allyl<sup>-</sup>, (R<sup>3</sup>-R<sup>7</sup>)-cyclopentadienyl<sup>-</sup>, wherein the radicals R<sup>3</sup> to R<sup>7</sup> are as defined above.

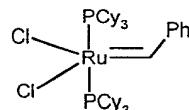
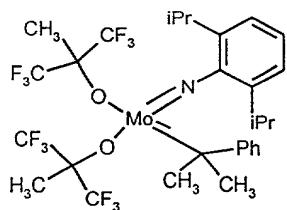
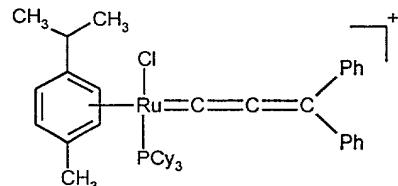
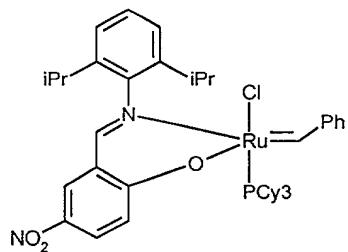
L<sup>1</sup> to L<sup>3</sup> are uncharged ligands that can be selected independently, in particular CO, CO<sub>2</sub>, R<sup>3</sup>NCO, R<sup>3</sup>R<sup>4</sup>C=CR<sup>5</sup>R<sup>6</sup>, R<sup>3</sup>C≡CR<sup>4</sup>, R<sup>3</sup>R<sup>4</sup>C=NR<sup>5</sup>, R<sup>3</sup>C≡N, R<sup>3</sup>OR<sup>4</sup>, R<sup>3</sup>SR<sup>4</sup>, NR<sup>3</sup>R<sup>4</sup>R<sup>5</sup>, PR<sup>3</sup>R<sup>4</sup>R<sup>5</sup>, AsR<sup>3</sup>R<sup>4</sup>R<sup>5</sup>, SbR<sup>3</sup>R<sup>4</sup>R<sup>5</sup>,

wherein the radicals R<sup>3</sup> to R<sup>5</sup> are as defined above;

m is 1 or 2.

Particularly preferred catalysts or catalyst precursors are compounds of the formulae (III) and (IV) in which L<sup>1</sup> and L<sup>2</sup> = PR<sup>3</sup>R<sup>4</sup>R<sup>5</sup>, where R<sup>3</sup> to R<sup>5</sup> are as defined above and very particularly preferred radicals of this type are aryl or alkyl, in particular secondary alkyl radicals or cycloalkyl radicals.

Very particular preference is given to using the following compounds as catalysts in the process of the invention:



where Cy = cyclohexyl, iPr = isopropyl, Ph = phenyl.

The catalysts can be used in isolated form or can be generated *in situ* in the reaction medium from catalyst precursors. The amounts of catalyst that are used in the process of the invention are generally from 0.001 to 15 mol%, based on the starting materials. The process of the 5 present invention is preferably carried out using from 0.1 to 12 mol% of catalyst, particularly preferably from 0.5 to 9 mol%, based on the starting materials.

The ionic liquids used in the process of the invention are salts or salt mixtures that are liquid in a temperature range from -20°C to 300°C.

10 In the process of the invention, preference is given to using ionic liquids that comprise aluminium halides in combination with at least one quaternary ammonium halide and/or at least one quaternary phosphonium halide.

15 As quaternary ammonium compounds, particular preference is given to using heterocyclic compounds that contain at least one nitrogen atom. These are, for example, pyridinium compounds or imidazolium compounds.

20 Very particularly preferred ionic liquids are aluminium chloride in combination with 1-methyl-3-butylimidazolium chloride, 1-methyl-3-ethylimidazolium chloride, N-butylpyridinium chloride and/or tetrabutylphosphonium chloride.

25 The process of the invention is preferably carried out using ionic liquids that comprise a combination of aluminium halide and quaternary ammonium halides and/or quaternary phosphonium halides in a molar ratio of (0.6 – 1) : 1. The molar ratio of aluminium halide to quaternary ammonium halide and/or quaternary phosphonium halide should never be greater than 1 since otherwise an excess of Lewis acid is present in the reaction mixture. This acidic reaction mixture leads to deactivation of the transition metal carbene catalysts.

Preference is also given to using ionic liquids that comprise ammonium hexafluorophosphate, ammonium tetrafluoroborate, ammonium tosylate or ammonium hydrogen sulphate or consist of ammonium hexafluorophosphate, ammonium tetrafluoroborate, 5 ammonium tosylate or ammonium hydrogen sulphate in the process of the invention.

Ionic liquids used are particularly preferably pyridinium hexafluorophosphate, 1-methyl-3-butyl hexafluorophosphate, pyridinium 10 tetrafluoroborate, pyridinium hydrogen sulphate or N-butylpyridinium hexafluorophosphate.

As ionic liquids in the process of the invention, it is also possible to use combinations of aluminium halide with mixtures of quaternary ammonium halides and/or quaternary phosphonium halides, or mixtures of ammonium hexafluorophosphates, ammonium tetrafluoroborates, 15 ammonium tosylates or ammonium hydrogen sulphates.

The process of the invention can be carried out in the presence of one or more additives, preferably a solvent, that, for example, makes it easier to separate the products from the ionic liquid and the catalyst present therein. In the presence of an additive and the ionic liquids, a 20 heterogeneous catalyst system is obtained when ionic catalysts or catalysts that dissolve preferentially in the ionic liquid are used. After the metathesis reaction is complete, the ionic phase comprising the catalyst can easily be separated from the additive and the reaction product present therein. The catalyst in the ionic liquid can be used for further metathesis 25 reactions without intermediate purification steps.

Such additives can be selected, for example, from among: phosphorus compounds, amines, perfluorinated compounds, metal 30 alkoxides and organic solvents. Suitable organic solvents are, in particular, halogenated hydrocarbons such as dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane or

trichloroethane, aromatic compounds such as benzene, toluene, xylene, cumene or halogenobenzenes, alkanes such as pentane, hexane or cyclohexane, esters such as tert-butylmethyl esters or acetic esters, ethers such as diethyl ether, tetrahydrofuran and dimethoxyethane, 5 amides such as dimethylformamide, antioxidants such as hydroquinones, acetone, dimethyl carbonate or alcohols.

Preferred additives for use in the process of the invention are C<sub>5</sub>-C<sub>20</sub>-alkanes, ethers and halogenated hydrocarbons.

10 Pentane, n-hexane, methyl tert-butyl ether or dichloromethane are very particularly preferably used in the process of the invention.

The process of the invention is preferably carried out at pressures in the range from 0.1 to 10 bar, particularly preferably at atmospheric pressure. However, the process of the invention can also be carried out at 15 subatmospheric pressures down to 0.01 bar and superatmospheric pressures up to 100 bar.

The process of the invention is usually carried out in a temperature range from -20°C to 200°C, preferably from 0°C to 150°C, very particularly preferably from 20°C to 100°C.

20 The cyclic compounds or polymers that can be prepared by the process of the invention can be further purified and processed with the aid of customary methods. The catalyst in the ionic liquid can be used for further metathesis reactions without intermediate purification steps.

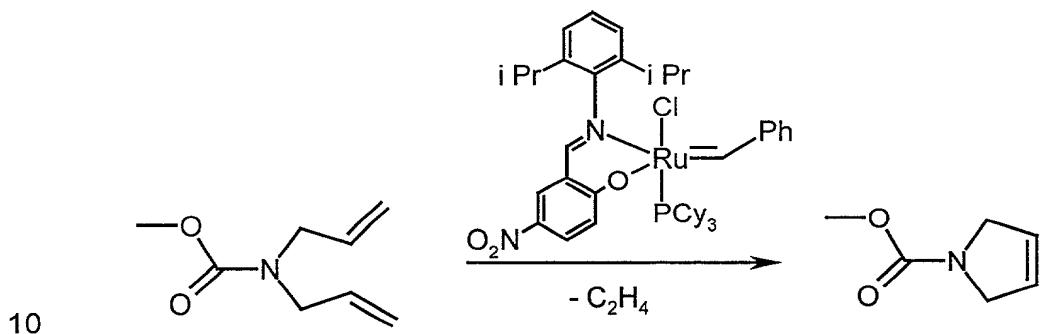
The invention is further illustrated but is not intended to be limited by 25 the following examples in which all parts and percentages are by weight unless otherwise specified.

### EXAMPLES

The examples below describe metathesis reactions in the presence of ionic liquids (and additives) under preferred conditions. However, they in no way restrict the scope of the present invention. The abbreviation Cy represents cyclohexyl, Ph represents phenyl, iPr represents isopropyl and TfO represents triflate.

#### Example 1

Preparation of N-carboxymethyl-2,5-dihydropyrrole

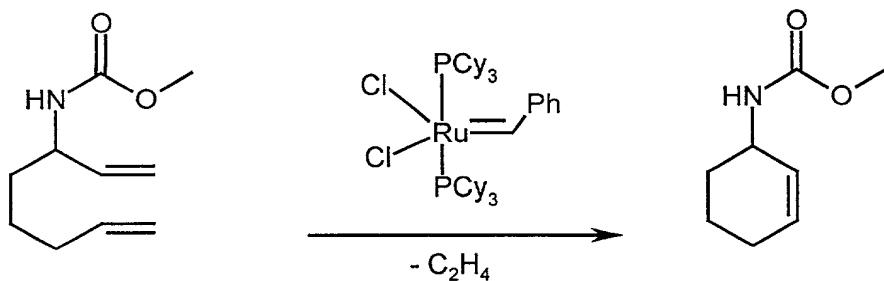


155 mg (1 mmol) of N-carboxymethyl-diallylamine and 17 mg of (tricyclohexylphosphine)-benzylidene-chloro-ruthenium(IV) 2-[(2,6-diisopropylphenyl)imino]methyl-4-nitro-phenoxide (2 mol%) were dissolved in a liquid mixture of 579 mg of 1-methyl-3-ethylimidazolium chloride (4 mmol) and 533 mg of aluminum trichloride (4 mmol) under an argon atmosphere. The mixture was covered with 3 ml of absolute n-hexane. It was allowed to react for 30 minutes at room temperature while stirring. After phase separation, the ionic phase was washed three times with n-hexane.

20 Analysis of the organic phase by gas chromatography indicated a proportion of 30% of N-carboxymethyl-2,5-dihydropyrrole product. Covering the catalyst phase once more with a solution of 155 mg (1 mmol) of N-carboxymethyl-diallylamine in 3 ml of n-hexane, another reaction time of 30 minutes and an analogous work-up gave a yield of 20% of N-carboxymethyl-2,5-dihydropyrrole.

Example 2

Preparation of N-carboxymethyl-3,4,5,6-tetrahydroaniline



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92 mg (0.5 mmol) of N-carboxymethyl-3-amino-1,7-octadiene and 4 mg of bis(tricyclohexylphosphine)-benzylidene-ruthenium(IV) dichloride (1 mol%) were dissolved in a liquid mixture of 586 mg of 1-methyl-3-ethylimidazolium chloride (4 mmol) and 533 mg of aluminium trichloride (4 mmol) under an argon atmosphere in a baked-out Schlenk tube. The mixture was allowed to react for two hours at 50°C. After an aqueous work-up, the mixture was filtered through a very short silica gel column (0.5 cm), washed four times with 1 ml each time of acetonitrile and evaporated.

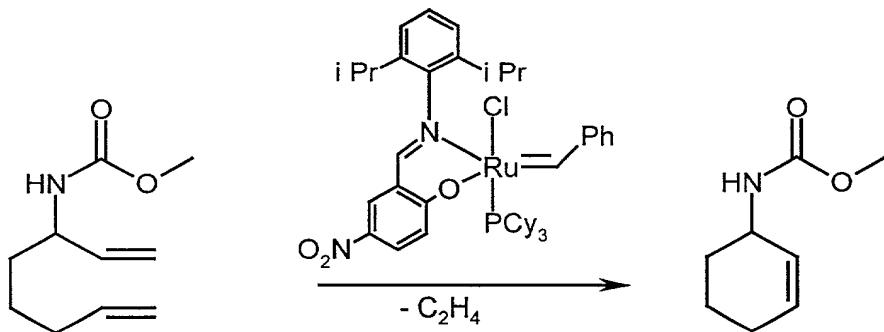
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Yield: 77 mg of N-carboxymethyl-3,4,5,6-tetrahydroaniline (0.49 mmol, 99% of theory).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 5.85 (1H, d, J = 9.0 Hz), 5.60 (1H, d, J = 9.0 Hz), 4.70 (1H, s), 4.20 (1H, s), 3.65 (3H, s), 1.98 (2H, m), 1.90 (1H, m), 1.62 (2H, m), 1.52 (1H, m).

Example 3

Preparation of N-carboxymethyl-3,4,5,6-tetrahydroaniline



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92 mg (0.5 mmol) of N-carboxymethyl-3-amino-1,7-octadiene and 10 mg of the ruthenium catalyst shown in the reaction scheme above, namely (tricyclohexylphosphine)-benzylidene-chloro-ruthenium-(IV) 2-[(2,6-diisopropylphenyl)imino]methyl-4-nitro-phenoxide, were dissolved in 1 ml

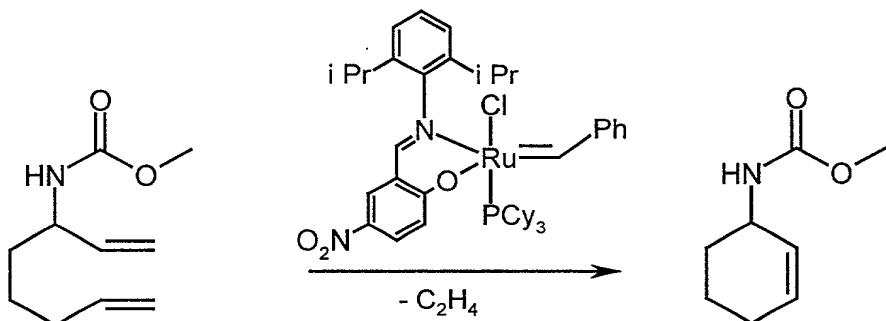
10 of absolute hexane and a mixture of 290 mg (2 mmol) of 1-methyl-3-ethylimidazolium chloride and 266 mg (2 mmol) of aluminium trichloride under an argon atmosphere in a baked-out Schlenk tube. The mixture was allowed to react for 3 hours at 50°C. For the work-up, the organic phase was pipetted off and the phase comprising the ionic liquid was washed twice with 2 ml each time of hexane. The combined hexane phases were evaporated. Finally, the mixture was filtered through a very short silica gel column (0.2 cm), washed once with 1 ml of acetonitrile and evaporated. The catalyst dissolved in the ionic liquid is available for a further reaction with substrate in hexane.

15

20 Yield: 74 mg of N-carboxymethyl-3,4,5,6-tetrahydroaniline (0.48 mmol, 96% of theory).

Example 4

Preparation of N-carboxymethyl-3,4,5,6-tetrahydroaniline



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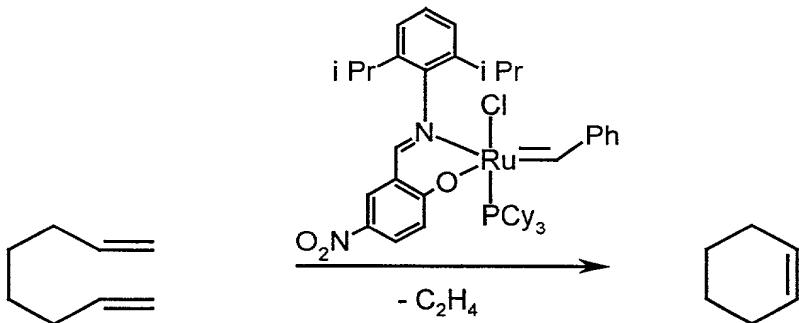
92 mg (0.5 mmol) of N-carboxymethyl-3-amino-1,7-octadiene and 4 mg of bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride (1 mol%) were dissolved in a liquid mixture of 684 mg of N-butylypyridinium chloride (4 mmol) and 533 mg of aluminium trichloride (4 mmol) under an argon atmosphere in a baked-out Schlenk tube. The mixture was allowed to react for two hours at 50°C. After an aqueous work-up, the mixture was filtered through a very short silica gel column (0.5 cm), washed four times with 1 ml each time of acetonitrile and evaporated.

10

Yield: 77 mg of N-carboxymethyl-3,4,5,6-tetrahydroaniline (0.49 mmol, 98% of theory).

Example 5

Preparation of tetrahydrobenzene



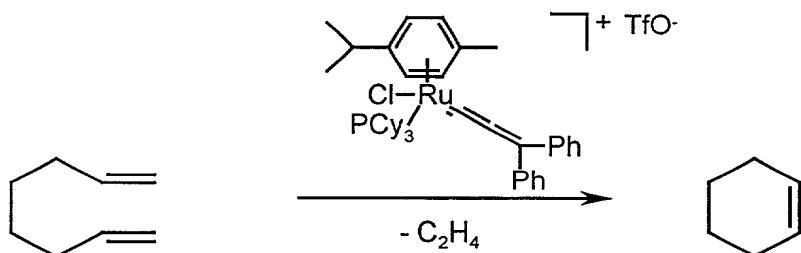
110 mg (1 mmol) of 1,7-octadiene and 17 mg of (tricyclohexylphosphine)-benzylidene-chloro-ruthenium-(IV) 2-[(2,6-diisopropylphenyl)imino]methyl-4-nitro-phenoxide (2 mol%) were dissolved in 3 ml of absolute pentane under an argon atmosphere in a baked-out Schlenk tube. A liquid mixture of 5 579 mg of 1-methyl-3-ethylimidazolium chloride (4 mmol) and 533 mg of aluminium trichloride (4 mmol) was added thereto. The mixture was allowed to react for 30 minutes at room temperature. For the work-up, the 10 organic phase was pipetted off and the phase comprising the ionic liquid was washed twice with 2 ml each time of pentane. The combined pentane phases were evaporated. The mixture was subsequently filtered through a very short silica gel column (0.2 cm), washed once with 1 ml of pentane and evaporated.

The yield of tetrahydrobenzene was determined by gas chromatography (internal standard: tetradecane) and was 99% of theory.

15 After covering the reaction solution once more with a mixture of 110 mg (1 mmol) of 1,7-octadiene in pentane, a reaction time of 30 minutes and subsequent phase separation, a yield of 63% of tetrahydrobenzene was obtained.

Example 6

20 Preparation of tetrahydrobenzene



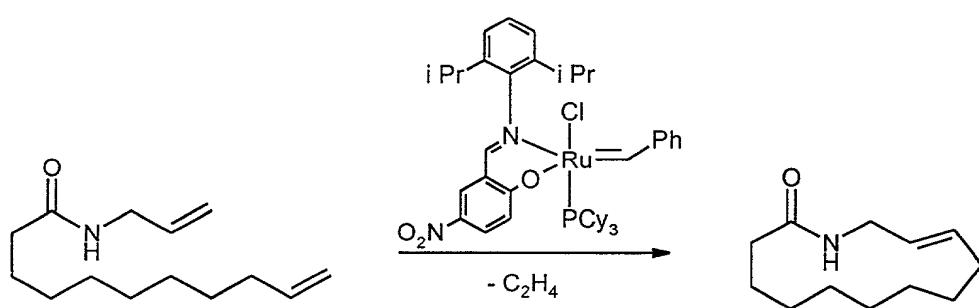
25 28 mg of 1,7-octadiene (0.25 mmol) were dissolved in a mixture of 345 mg (2 mmol) of 1-methyl-3-butylimidazolium chloride and 266 mg (2 mmol) of aluminium trichloride under an argon atmosphere in a 20 ml Schlenk tube.

11 mg of the cationic catalyst described in the reaction scheme above (5 mol%) were added thereto. The reaction solution was covered with 3 ml of methyl tert-butyl ether. The mixture was allowed to react for 90 minutes at a temperature of 40°C and the organic phase was then separated off. The 5 ionic phase was extracted three times with methyl tert-butyl ether.

Gas chromatography found a content of 32% of the desired tetrahydrobenzene. This result was obtained again in a subsequent second metathesis reaction using the same ionic phase.

Example 7

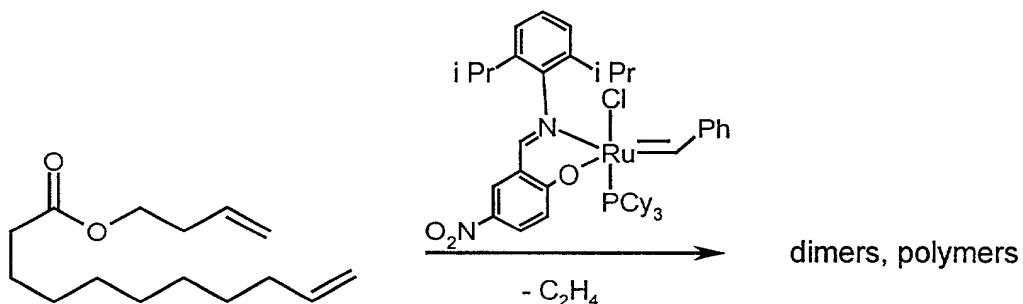
10 Preparation of aminocyclotridec-11-en-2-one



15 58 mg (0.25 mmol) of 10-undecenoyl-allylamide and 10 mg of (tricyclohexylphosphine)-benzylidene-chloro-ruthenium-(IV) 2-[(2,6-diisopropylphenyl)imino]methyl-4-nitro-phenoxide (5 mol%) were dissolved in 3 g of 1-methyl-3-butylimidazolium hexafluorophosphate. The mixture was allowed to react at 40°C for 14 hours. The ionic phase was extracted with dichloromethane. After filtration through a very short silica gel column (length about 0.5 cm), about 80% of the desired product were obtained (yield determined by means of gas chromatography). The trans/cis ratio of the product is about 5:1.

Example 8

Metathesis of buten-4-yl 10-undecenoate

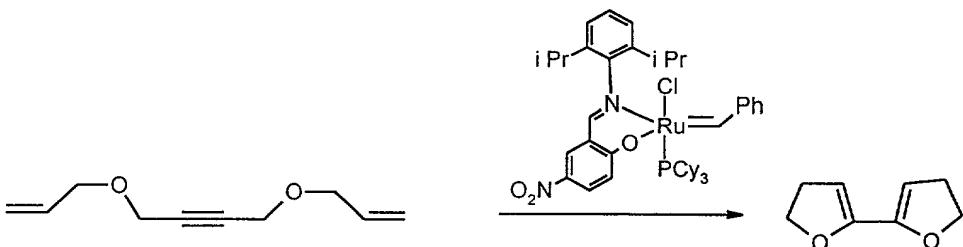


5

238 mg of buten-4-yl 10-undecenoate and 8 mg of (tricyclohexylphosphine)-benzylidene-chloro-ruthenium-(IV) 2-[(2,6-diisopropylphenyl)imino]methyl-4-nitro-phenoxide (8 mol%) were dissolved in a mixture of 580 mg (4 mmol) of 1-methyl-3-ethylimidazolium chloride and 533 mg of aluminium trichloride (4 mmol). The mixture was covered with 40 ml of absolute pentane. It was allowed to react for five hours at room temperature while mixing well. Apart from a large percentage of polymer, about 10% of dimers of the diene used were obtained.

Example 9

15 Preparation of 3,3'-bis-2,5-dihydrofuranyl



20 166 mg of 1,4-bis(oxypropen-2-yl)but-2-ine together with 41 mg of (tricyclohexylphosphine)-benzylidene-chloro-ruthenium-(IV) 2-[(2,6-diisopropylphenyl)imino]methyl-4-nitro-phenoxide (5 mol%) were dissolved

in a liquid mixture of 2.31 g of 1-methyl-3-ethylimidazolium chloride (16 mmol) and 2.13 g of aluminium trichloride (16 mmol) under an argon atmosphere in a baked-out Schlenk tube. The mixture was allowed to react for 18 hours at 40°C. For the work-up, the ionic phase was washed a number of times with toluene. The combined toluene extracts were filtered through a very short silica gel column (0.5 cm). The column was washed four times with 10 ml each time of toluene and the filtrates were evaporated.

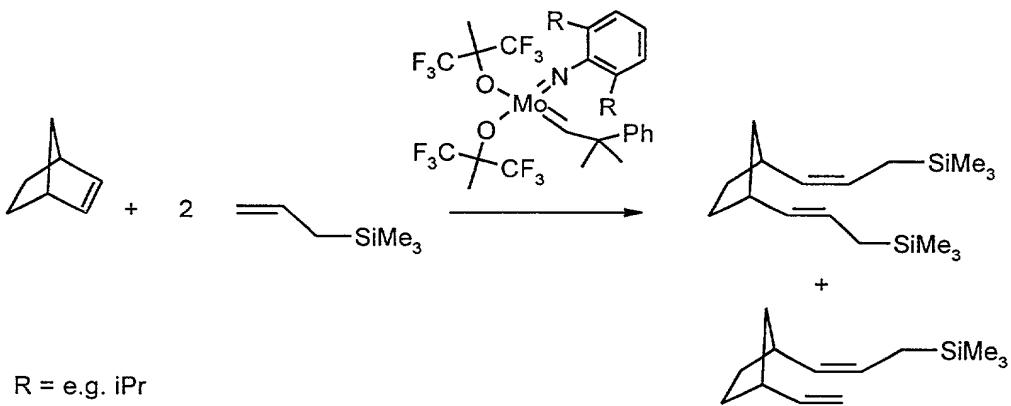
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Yield: 120 mg of 3,3'-bis-2,5-dihydrofuranyl (87% of theory).

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#### Example 10

Preparation of 1,3-di(3-trimethylsilyl-propen-1-yl)-cyclopentane and 1-(3-trimethylsilyl-propen-1-yl)-3-vinyl-cyclopentane



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47 mg of norbornene (0.5 mmol) and 126 mg of allyltrimethylsilane (1.1 mmol) were dissolved in a mixture of 289 mg (2 mmol) of 1-methyl-3-ethylimidazolium chloride and 266 mg (2 mmol) of aluminium trichloride under an argon atmosphere. 10 mg (3 mol%) of the molybdenum catalyst shown above were subsequently added to this reaction mixture. The resulting mixture was covered with 3 ml of n-hexane and the mixture was allowed to react for one hour at room temperature.

20

After separating off the organic phase and extracting the ionic phase with n-hexane and then combining the organic extracts, the combined extracts were analysed by gas chromatography. Yield of disilylated product, viz. 1,3-di(3-trimethylsilyl-propen-1-yl)-cyclopentane: about 60% of theory; yield of monosilylated product, viz. 1-(3-trimethylsilyl-propen-1-yl)-3-vinyl-cyclopentane: about 20% of theory. In addition, polymeric products were found. No starting material could be detected.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

20 10

WHAT IS CLAIMED IS:

1. A process for preparing cyclic and/or polymeric compounds comprising the step of subjecting a starting material to metathesis in the presence of a catalyst component comprising a member selected from the group consisting of homogeneous catalysts and heterogeneous catalysts,  
5 wherein the starting material comprises a member selected from the group consisting of compounds containing at least two functional groups in the form of a substituted or an unsubstituted alkene or alkyne units;
- 10 wherein the catalyst component comprises a member selected from the group consisting of transition metal carbenes and transition metal compounds that form transition metal carbenes under the reaction conditions or transition metal salts in combination with an alkylating agent; and  
15 wherein the metathesis is carried out in the presence of ionic liquids.
2. The process of Claim 1, wherein the polymeric compounds comprise a member selected from the group consisting of homopolymers, copolymers and block copolymers.
3. The process of Claim 1, wherein the cyclic compounds  
20 comprise a member selected from the group consisting of carbocyclic compounds and heterocyclic compounds having ring sizes of  $\geq 5$  ring atoms.
4. The process of Claim 1, wherein the starting materials contain, apart from the functional groups participating in the metathesis  
25 reaction, at least one further substituent that is inert in the metathesis reaction and/or a heteroatom.
5. The process of Claim 4, wherein the substituents or heteroatoms mentioned are comprise a member selected from the group consisting of branched or unbranched alkyl radicals, aromatic or non-aromatic carbocyclic rings, carboxylic acids, esters, ethers, epoxides, silyl ethers,  
30

thioethers, thioacetals, anhydrides, imines, silylenol ethers, ammonium salts, amides, nitriles, perfluoroalkyl groups, geminal dialkyl groups, alkynes, alkenes, halogens, alcohols, ketones, aldehydes, carbamates, carbonates, urethanes, sulphonates, sulphones, sulphonamides, nitro groups, organosilane units, metal centres and oxygen-containing heterocycles, nitrogen-containing heterocycles, sulphur-containing heterocycles, and phosphorus-containing heterocycles.

6. The process of Claim 5, wherein the starting materials used comprise  $\alpha,\omega$ -dienes that may contain a member selected from the group containing at least one further substituent that is inert in the metathesis reaction and a heteroatom,

wherein these substituents or heteroatoms comprise a member that is selected from the group consisting of branched alkyl radicals, unbranched alkyl radicals, aromatic carbocyclic rings, non-aromatic carbocyclic rings, carboxylic acids, esters, ethers, epoxides, silyl ethers, thioethers, thioacetals, anhydrides, imines, silylenol ethers, ammonium salts, amides, nitriles, perfluoroalkyl groups, geminal dialkyl groups, alkynes, alkenes, halogens, alcohols, ketones, aldehydes, carbamates, carbonates, urethanes, sulphonates, sulphones, sulphonamides, nitro groups, organosilane units, metal centres and oxygen-containing heterocycles, nitrogen-containing heterocycles, sulphur-containing heterocycles and phosphorus-containing heterocycles.

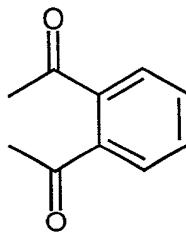
7. The process of Claim 6, wherein the  $\alpha,\omega$ -dienes used bear a substituent  $\text{NRR}^1$  in the  $\alpha$  position to a double bond, wherein

25            R        is an organic substituent,

$\text{R}^1$     is tert-butyl,  $\text{P}(\text{R})_2$ ,  $\text{P}(\text{R}^2)_2$ ,  $\text{COR}$ ,  $\text{SO}_2\text{PhR}$ ,  $\text{COOR}$  or  $\text{CONRR}^2$ ,

$\text{R}^2$     is alkyl or phenyl,

R and R<sup>1</sup> together form



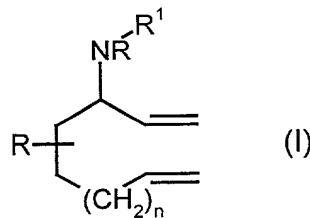
and

said  $\alpha,\omega$ -dienes may also bear at least one further substituent R in any other position in the molecule with the exception of the  $\alpha$  position.

5        8. The process of Claim 7, wherein R comprises a member selected from the group consisting of hydrogen, fused or unfused aryl, alkyl, CN, COOR<sup>2</sup> or halogen.

9. The process of Claim 7, wherein the  $\alpha,\omega$ -dienes used have the formula (I)

10



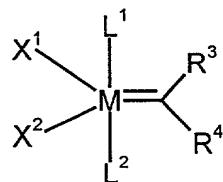
wherein R, R<sup>1</sup> and R<sup>2</sup> are as defined in claim 7 and n is 1, 2, 3 or 4, preferably 1 or 2, particularly preferably 1.

15        10. The process of Claim 9, wherein n is 1 or 2.

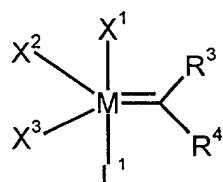
11. The process of Claim 10, wherein n is 1.

12. The process of Claim 7, wherein the  $\alpha,\omega$ -dienes used are diallylamine or 3-amino-1,7-octadiene, particularly preferably in their N-carboxymethyl-protected form, or 1,7-octadiene, 10-undecenoyl-allyl-amide, 1,4-bis-oxypropen-2-yl-but-2-ine or buten-4-yl 10-undecenoate.

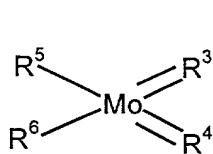
20        13. The process of Claim 1, wherein the catalysts used are compounds of the formulae (III) to (VI), wherein M is ruthenium or osmium



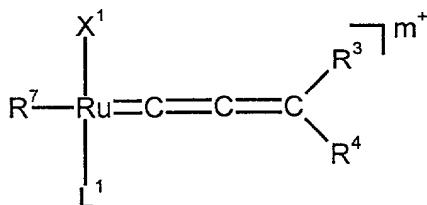
(III)



(IV)



(V)



(VI)

and

R<sup>3</sup> to R<sup>7</sup> are radicals are selected from the group consisting of

5 hydrogen, C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>3</sub>-C<sub>8</sub>-cycloalkyl, C<sub>2</sub>-C<sub>20</sub>-alkenyl, C<sub>2</sub>-C<sub>20</sub>-alkinyl, C<sub>6</sub>-C<sub>18</sub>-aryl, C<sub>1</sub>-C<sub>20</sub>-carboxylate, C<sub>1</sub>-C<sub>20</sub>-alkoxy, C<sub>2</sub>-C<sub>20</sub>-alkenyloxy, C<sub>2</sub>-C<sub>20</sub>-alkinylloxy, C<sub>6</sub>-C<sub>18</sub>-aryloxy, C<sub>2</sub>-C<sub>20</sub>-alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub>-alkylthio, C<sub>1</sub>-C<sub>20</sub>-alkylsulphonyl and C<sub>1</sub>-C<sub>20</sub>-alkylsulphinyl, N-aryl; wherein in each case

10 unsubstituted or substituted by C<sub>1</sub>-C<sub>12</sub>-alkyl, perfluoroalkyl, halogen, C<sub>1</sub>-C<sub>5</sub>-alkoxy or C<sub>6</sub>-C<sub>18</sub>-aryl;  
and wherein the radicals R<sup>3</sup> to R<sup>7</sup> may be linked to one another in cyclic compounds,

$X^1$  to  $X^3$  are anionic ligands comprise a member that is selected from the group consisting of  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $CN^-$ ,  $SCN^-$ ,  $R^3O^-$ ,  $R^3R^4N^-$ ,  $(R^3-R^7)$ -allyl $^-$ ,  $(R^3-R^7)$ -cyclopentadienyl $^-$ , wherein the radicals  $R^3$  to  $R^7$  are as defined above,

$L^1$  to  $L^3$  are uncharged ligands comprise a member that is selected from the group consisting of  $CO$ ,  $CO_2$ ,  $R^3NCO$ ,  $R^3R^4C=CRR^5R^6$ ,  $R^3C\equiv CR^4$ ,  $R^3R^4C\equiv NR^5$ ,  $R^3C\equiv N$ ,  $R^3OR^4$ ,  $R^3SR^4$ .

NR<sup>3</sup>R<sup>4</sup>R<sup>5</sup>, PR<sup>3</sup>R<sup>4</sup>R<sup>5</sup>, AsR<sup>3</sup>R<sup>4</sup>R<sup>5</sup>, SbR<sup>3</sup>R<sup>4</sup>R<sup>5</sup>, wherein the radicals R<sup>3</sup> to R<sup>5</sup> are as defined above

and

m is 1 or 2.

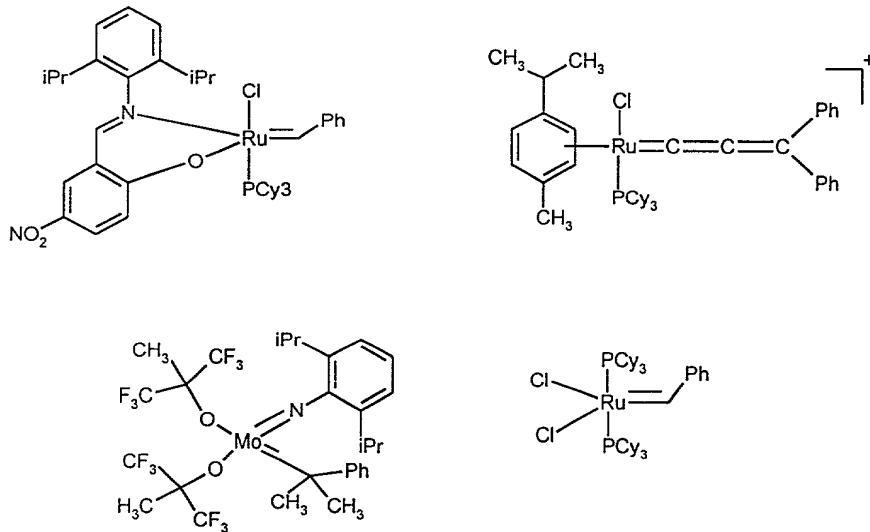
5 14. The process of Claim 13, wherein the catalysts or catalyst precursors used are compounds of the formula (III) and/or (IV) wherein L<sup>1</sup> and L<sup>2</sup> = PR<sup>3</sup>R<sup>4</sup>R<sup>5</sup>, wherein R<sup>3</sup> to R<sup>5</sup> are as defined above.

15. The process of Claim 14, wherein R<sup>3</sup> to R<sup>5</sup> comprise a member selected from the group consisting of aryl or alkyl groups.

10 16. The process of Claim 15, wherein R<sup>3</sup> to R<sup>5</sup> comprise a member selected from the group consisting of secondary alkyl radicals and cycloalkyl radicals.

17. The process of Claim 14, wherein the catalysts used are the following compounds:

15



18. The process of Claim 1, wherein the ionic liquids used comprise a member selected from the group consisting of ammonium -

20 hexafluorophosphate, ammonium tetrafluoroborate, ammonium tosylate, ammonium hydrogen sulphate and salt mixtures comprising aluminium

halides in combination with at least one quaternary ammonium halide and/or at least one quaternary phosphonium halide.

19. The process of Claim 13, wherein the ionic liquids used comprise a member selected from the group consisting of pyridinium hexafluorophosphate, pyridinium tetrafluoroborate, pyridinium hydrogen sulphate, 1-methyl-3-butylimidazolium hexafluorophosphate or combinations of aluminium chloride with 1-methyl-3-butylimidazolium chloride, 1-methyl-3-ethylimidazolium chloride, N-butylpyridinium chloride and tetrabutylphosphonium halide.

20. The process of Claim 1, wherein the ionic liquids used comprise a member selected from the consisting of combinations of aluminium halide with mixtures of quaternary ammonium halides, quaternary phosphonium halides, and mixtures of ammonium hexafluorophosphate, ammonium tetrafluoroborate, ammonium tosylate and ammonium hydrogen sulphate.

21. The process of Claim 1, wherein the reaction medium further comprises an additive that is selected from the group consisting of phosphorus compounds, amines, perfluorinated compounds, metal alkoxides and organic solvents.

METATHESIS IN THE PRESENCE OF IONIC LIQUIDS

ABSTRACT OF THE DISCLOSURE

A process for preparing cyclic and/or polymeric compounds by metathesis of starting materials that contain at least two functional groups in the form of substituted or unsubstituted alkene or alkyne units.

2025 RELEASE UNDER E.O. 14176

**COMBINED DECLARATION AND POWER OF ATTORNEY**

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**Metathesis in the presence of ionic liquids**

the specification of which is attached hereto,

or was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

<u>19909600.7</u> (Number)	<u>Germany</u> (Country)	<u>March 05, 1999</u> (Month/Day/Year Filed)
<u>19927912.8</u> (Number)	<u>Germany</u> (Country)	<u>June 18, 1999</u> (Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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